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Automatic measurements of ten kinds of gases using ball SAW gas chromatograph

ボール SAW ガスクロマトグラフを用いた 10 種類のガスの連続測定

Toshihiro Sakamoto[1,3†], Shingo Akao[1,2,3], Takamitsu Iwaya[1,2], Toshihiro Tsuji[1,3], Noritaka Nakaso[1,2,3], and Kazushi Yamanaka[1,3] ([1]School of Eng., Tohoku Univ., [2]Toppan Printing Co., Ltd., [3]JST,CREST)
坂本 俊裕[13‡], 赤尾 慎吾[123], 岩谷 隆光[13], 辻 俊宏[13], 中曽 教尊[123], 山中 一司[13]
([1]東北大 工; [2]凸版印刷, [3]JST,CREST)

1. Introduction

Health hazards of workers are reported in environments like factories. Thus, the Japan society for occupational health listed gases causing health hazards for exposed workers, and set their acceptable concentration limits [1]. Volatile organic compounds (VOCs) are included in them (ex. Toluene, 50 ppm).

Although gas chromatograph (GC) is used for analysis of such gases, conventional GCs are too heavy to carry, and development of portable GC is demanded. We have developed ball surface acoustic wave (SAW) GC [2,3] using the ball SAW sensor where SAW makes multiple roundtrip without diffusing by the diffraction [4,5] and a micro separation column fabricated by micro electro mechanical system (MEMS) technology [2].

In GC, heavy gases have long retention time in the column and light gases have short one. When fast analysis of multiple gases containing heavy and light gases is required, the temperature programming method is used [6], shortening the retention time of heavy gases by heating the column in the later part of the analysis. However, this method is unsuitable for portable GC because of power consumption of the heater.

In this study, we show the probability of gas concentration monitoring in working environments by developing ball SAW GC using forward flush (FF) method [3] which is the fast analysis method without a heater by taking advantage of nondestructive nature of ball SAW sensor and analyzing 10 kinds of gases using it.

2. Concept of forward flush (FF) method

The principle of FF method is shown in Fig.1 [3]. It is the fast multiple gases analysis method by switching flow paths between serial and parallel using strong retention column (CL1), weak retention column (CL2) and 2 ball SAW sensor (BS1,2). At first, sample gas is injected at the state where CL1-BS1-CL2-BS2 are serially connected (Fig1(a)). Automatically sampled gases A~G are flown into CL1. While heavy gases D~G are retained by CL1, light gases are not retained but passed through to BS1 which detect mixture of light gases A~C nondestructively. Three way valves switches flow paths after light gases A~C flow into CL2(Fig1(b)). CL1-BS1 and CL2-BS2 are connected parallel. Retained gases D~G are separated by CL1 and then detected by BS1 while gases A~C are separated by CL2 and detected by BS2. This method has a low power consumption without heaters.

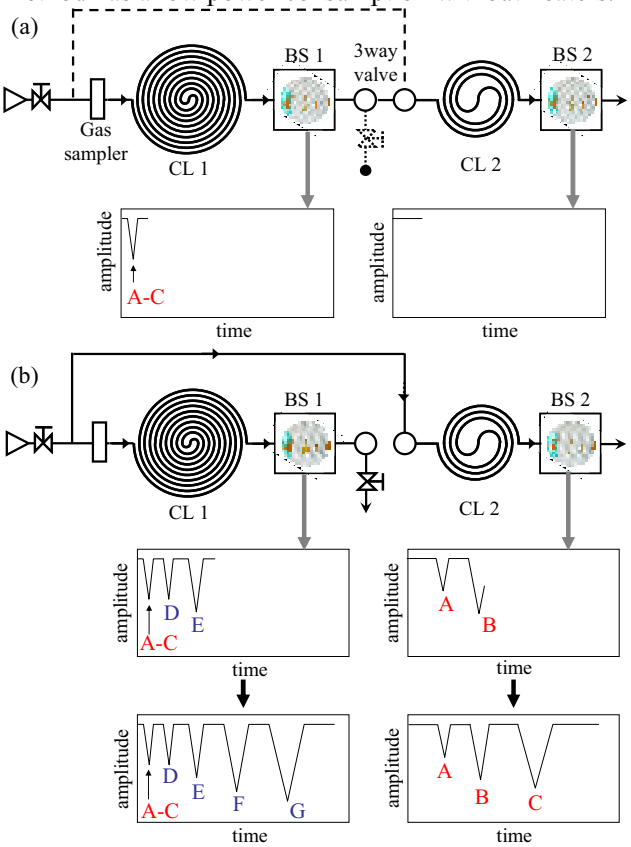

Fig.1 Principle of forward flush (FF) method
(a) serial connection (b) parallel connection

3. Linearity of sensor response to gas concentration

A plot of butanol gas concentration vs. deay time change of ball SAW sensor is shown in Fig.2, whose sensitive film is Siponate DS-10 coated by the off-axis spin-coating method [7]. The linearity of sensor response to ppm order gas concentration in working environments is verified. Also, the limit of detection

estimated with twice of noise level was 200 ppb.

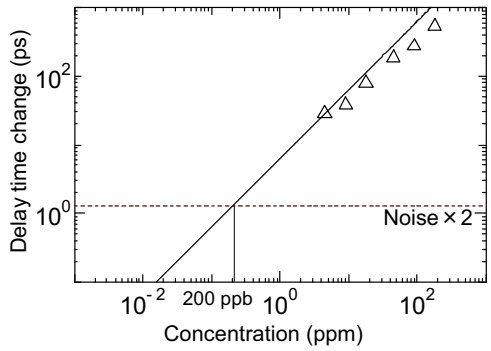

Fig.2 Gas concentration of butanol vs. sensor response

4. Measurements of 10 kinds of gases

Ball SAW GC with the FF method is shown in Fig. 3., with sizes of 240×180×100 mm. Valves for gas sampler and the FF method are automated by computerized control. Metal open tube MEMS column [8] with the benefit of low cost and high robustness, developed for the first time in our lab is used as CL2.

Chromatograms of 10 kinds of gases containing VOCs are shown in Fig.4, with concentrations of 1000 ppm. Separation and detection of ten kinds of gases were succeeded at room temperature (26 ℃), with 6 kinds at BS1 and 4 kinds at BS2

Fig. 3 Ball SAW GC with the FF methd

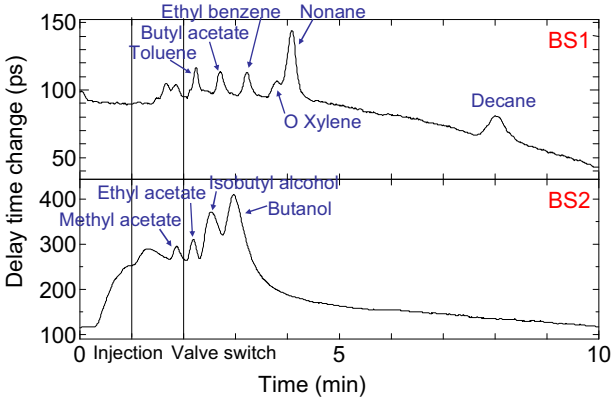

Fig. 4 Automatic measurement of 10 kinds of gases at room temperature using ball SAW GC

5. Measurment accuracy of butanol

A plot of time vs. delay time change is shown in Fig.5, obtained by periodic measurements of 90.5 ppm butanol standard gas, using a ball SAW GC with single column and sensor. The resolution in terms of gas concentration is shown in Table 1, evaluated with the RMS fluctuation (ps) from the average responses in Fig.5. The measurement resolution was 3.5 ppm and its ratio to the acceptable concentration limit (50 ppm) was 14. Also, the butanol concentration at the sensor estimated from the noise level in the chromatogram (Fig. 4) was 400 ppb, comparable to limit of detection in Fig.2 [7] .

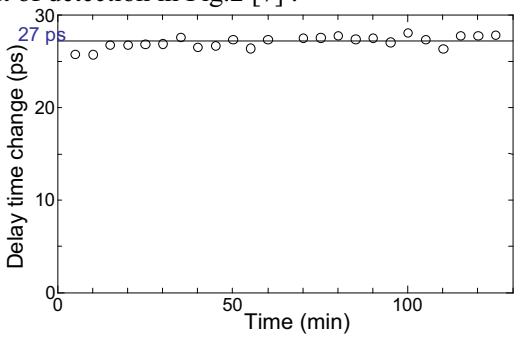

Fig. 5 The plot of time vs. sensor response to 90.5 ppm butanol

Table 1 Resolution and acceptable concentration of butanol achieved by periodic measurements

Average of responce(ps)	RMS(ps)	Resolution(ppm)	Acceptable concentration(ppm)
27	0.95	3.5	50

6. Conclusion

Measurement of 10 kinds of gases using ball SAW GC without a heater was demonstrated and the possibility for low power consumption needed in portable GC was verified. The measurement resolution was 3.5 ppm and its ratio to the acceptable concentration limit of butanol (50 ppm) was 14. This result shows the possibility of realizing multiple gases monitoring in working environments by setting threshold levels of acceptable concentration to each gas.

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